Molecular AND and INHIBIT Gates Based on Control of Porphyrin Fluorescence by Photochromes

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Abstract: A molecular triad consisting of a porphyrin (P) covalently linked to two photochromes – one from the dihydroindolizine family (DHI) and one from the dihydropyrene family (DHP) - has been synthesized and found to act as either a molecular AND logic gate or an INHIBIT gate, depending on the inputs and initial state of the photochromes. The basis of these functions is quenching of porphyrin fluorescence (output of the gates) by the photochromes. The spiro form of DHI does not quench porphyrin fluorescence, whereas its betaine isomer strongly quenches by photoinduced electron transfer. DHP also quenches porphyrin fluorescence, but its cyclophanediene isomer does not. The triad has been designed using suitable energetics and electronic interactions, so that although these quenching phenomena may be observed, independent isomerization of the attached photochromes still occurs. This makes it possible to switch porphyrin fluorescence on or off by isomerization of the photochromes using various combinations of inputs such as UV light, red light, and heat.

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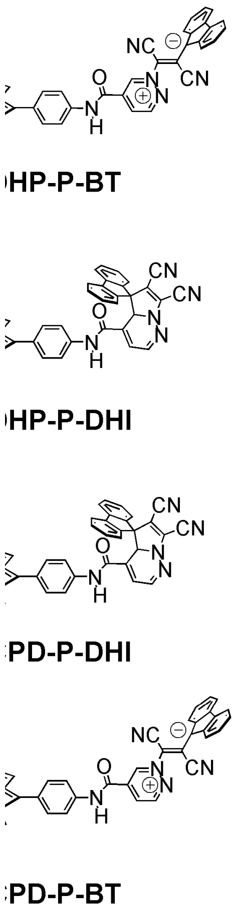
Introduction

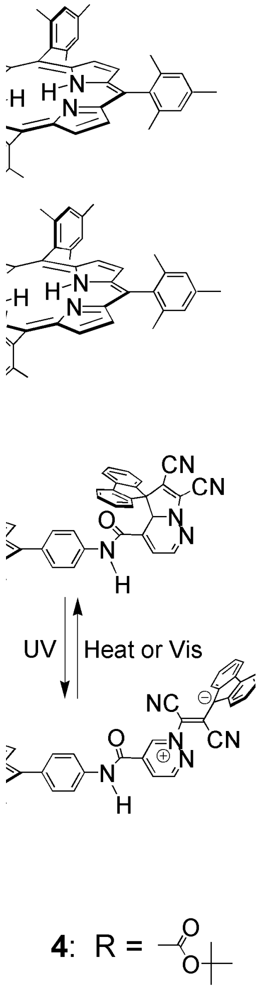
Silicon-based computers carry out mathematical operations using Boolean logic elements. The idea of performing such operations using molecules as switching elements is scientifically interesting and may have technological potential.[1-4] A variety of molecule-based systems capable of Boolean logic (AND gates, OR gates, etc.) have been reported.[5-23] In the vast majority of these, at least one of the inputs of the logic gate requires physical addition of a chemical species that diffuses to a molecule and carries out a reaction, changing molecular structure. Logic gates with chemical inputs require fluid solutions, and their speed is limited by the time required for material transfer, diffusion, and the speed of bimolecular chemical reactions. Molecule-based logic gates with optical inputs and outputs do not require access for chemicals or wires, and can in principle operate on a much faster time scale and in rigid or semi-rigid media. We have been interested in investigating logic elements that employ photochromic molecules whose photoisomerization subsequently switches on or off photoinduced electron transfer from a covalently-linked chromophore. In addition to a number of simple switches based on porphyrin-containing systems linked to spiropyrans,[24] dithienylethenes,[25] dihydropyrenes,[26] and dihydroindolizines,[27] we have recently reported a photonic double-throw switch,[28] and a half-adder.[23] In these molecules, the switching



ms of triad **1**.

elements are light or heat (which can be supplied by an IR laser), and the switched output is related to photoinduced electron transfer (formation of a charge-separated state, fluorescence quenching, etc.).

We now report the synthesis and study of triad **1** (Figure 1), which consists of a tetraarylporphyrin (P) linked to both a substituted dihydropyrene (DHP) photochrome and a photochrome of the dihydroindolizine (DHI) family based on pyrrolo[1,2-b]pyridazine. In spite of the nearby porphyrin chromophore and the resultant possibilities for quenching of photochrome photoisomerization due to electronic perturbation, energy transfer or photoinduced electron transfer, both of the photochromes may be photoisomerized. DHP may be isomerized to the open, cyclophane diene (CPD) using red light (590 – 900 nm), and CPD returns to the DHP isomer under irradiation with UV light (366 nm or 254 nm). Irradiation with UV (366 nm) opens the DHI moiety to the betaine (BT) isomer, which may be isomerized back to DHI thermally, including by irradiation with an IR laser at 1064 nm. Thus, the molecule may exist in four isomeric forms (Figure 1): DHP-P-BT, DHP-P-DHI, CPD-P-DHI and CPD-P-BT. As discussed below, by using various combinations of initial states and photonic or thermal inputs, the molecule may be made to function as either an AND gate or an INHIBIT gate. These results demonstrate the feasibility of implementing AND and INHIBIT logic functions in a molecule using light for input and output. However, the performance of the system has not been optimized, and any practical application would require overcoming problems of photostability and relatively slow switching times.



del compounds **2** –

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Experimental Section

Spectroscopy. All samples were dissolved in freshly-distilled 2-methyltetrahydrofuran and deoxygenated by bubbling with Ar for 20 min prior to study unless otherwise noted. Steady-state and time-based ground-state absorption measurements were performed using a Shimadzu UV-3101PC UV-vis-NIR spectrometer. Steady-state fluorescence emission spectra were determined using a Photon Technology International MP-1 fluorimeter, and corrected for detection system response as a function of wavelength. Excitation was from a 75 W xenon lamp and single-grating monochromator. Fluorescence was detected at a 90º angle to the excitation beam via a single-grating monochromator and an R928 photomultiplier tube having S-20 spectral response and operating in the single photon counting mode. Fluorescence decay measurements were performed on optically dilute (ca. 1×10^{-5} M) samples by single-photon timing. The excitation source was a cavity-dumped Coherent 700 dye laser pumped by a frequency-doubled Coherent Antares 76s Nd:Yag laser. The instrument response function was 35 - 60 ps, as measured at the excitation wavelength for each decay experiment with Ludox AS-40.[29]

The photoisomerization reactions of the DHI and the DHP photochromes were performed in the UV using a UVP UV lamp Model UVGL-25 (254 nm 700 μW/cm^2, and 366 nm 1.5 mW/cm^2) or in the visible with a Xe/HgXe-lamp (ORIEL Corp. Model 66028). Before sample illumination with the Xe-lamp, the IR portion of the light was reduced by double IR filters (OD=1.8 and OD=2.3 at 900 and 970 nm, respectively). Furthermore, a cut-off filter was used to remove wavelengths shorter than 590 nm. The power density of the resulting light was ≈33 mW/cm^2.

Isomerization of BT to DHI was accomplished either by heating the sample in a temperature block at 55° C, or by using light from the first harmonic of a Continuum Surelight Nd:YAG laser (1064 nm, 5 ns pulses, 10 Hz repetition rate, 500 mW average power). As the BT chromophore does not have electronic transitions in this wavelength region, this isomerization is essentially thermally driven. BT may also be isomerized to DHI using visible light at high intensity, but this method was not employed in this work.

Synthesis. The syntheses of model compounds **2** (DHP-P),[26] **3** (P-DHI)[27] and **4** (Figure 2)[28] have been previously reported.

Triad 1. Dyad **4** (30 mg, 0.026 mmol) was dissolved in 4 mL of distilled dichloromethane and 8 μL of triethylsilane and stirred with 1.8 mL of trifluoroacetic acid for 5 h. The reaction mixture was then diluted with dichloromethane washed with water until the wash water was neutral. The organic layer was evaporated at reduced pressure, and the residue was dissolved in 3.5 mL of dichloromethane and 10 μL of N-methyl morpholine. After cooling the resulting solution to 0° C, 4.5 mg (0.026 mmol) of 2-chloro-4,6-dimethoxy-1,3,5-triazine was added, with stirring. The reaction mixture was warmed to room temperature after 10 min and stirring was continued until TLC (1% acetone/dichloromethane) indicated that all the acid had been consumed. A 4-mg portion of dimethylaminopyridine was then added, followed by 3-{4'-(2',7'-di-*tert*-butyl-*trans*-12c',12d'-dimethyl-12c',12d'-dihydrobenzo[*e*]pyrenyl}prop-2-ynol[26] (11 mg, 0.004 mmol), and the reaction mixture was stirred for 1 h. The mixture was diluted with dichloromethane and washed 3 times with water, then kept overnight at -80° C. The following day the dichloromethane was evaporated and the residue chromatographed (silica gel, 30% ethyl acetate/hexanes) to give 6.0 mg of product (0.0039 mmol, 16%). ^{1}H NMR (500 MHz, CD_3Cl) δ -2.65 (2H, s, porphyrin N-H), -1.41 (3H, s, dihydropyrene $-CH_3$), -1.39 (3H, s, dihydropyrene $–CH_3$), 1.50 (9H, s, *t*-BuH), 1.56 (9H, s, *t*-BuH), 1.82 (12H, s, mesityl-CH_3), 2.62 (6H, s, mesityl-CH_3), 5.52 (2H, s, $-CH_2-$), 5.53 (1H, d, J = 2 Hz, pyridazine CH), 5.77 (1H, m, pyridazine C=CH-), 7.24 (1H, s, DHP Ar-H) 7.29 (4H, s, mesityl Ar-H), 7.43 (1H, s, DHP Ar-H) 7.44-7.65 (9H, m, fluorene Ar-H, DHP Ar-H, amide N-H), 7.70 (1H, d, J = 2 Hz) pyridazine N=CH-), 7.79 (2H, d, J = 8 Hz, meso Ar-H), 7.87-7.91 (2H, m, fluorene Ar-H), 8.00 (1H, s, DHP Ar-H), 8.14 (2H, d, J = 8 Hz, meso Ar-H), 8.25 (1H, m, DHP Ar-H) 8.30 (1H, m, DHP Ar-H), 8.34 (2H, d, J = 8 Hz, meso Ar-H), 8.54 (2H, d, J = 8 Hz, meso Ar-H) 8.65-8.76 (10 H, m, β-pyrrole CH, DHP Ar-H); MALDI-TOF calcd 1534.70 obsd 1504.64 (product minus two DHP-Me).

Results and Discussion

Model Compounds. In order to interpret and understand the results for **1**, the previously-reported photochemical behavior of model DHP-P dyad **2** and model P-DHI dyad **3** will be briefly reviewed.

Time-resolved fluorescence and transient absorption measurements[26] of the CPD-P form of dyad **2** in 2-methyltetrahydrofuran reveal that the porphyrin first excited singlet state of **2o** has a lifetime of 13.3 ns, which is very similar to that of porphyrin model compounds in deoxygenated solutions. Thus, the porphyrin first excited singlet state is not quenched by the CPD moiety, and decays by the usual pathways of intersystem crossing, internal conversion and fluorescence. Irradiation of the molecule with UV light at 254 nm converts most of the sample to the DHP-P form **2c**. Under these conditions two exponential emission components were observed at 650 nm, where essentially all of the emission is due to the porphyrin (with 590 nm excitation). The lifetimes are 1.76 ns (80%) and 13.0 ns (20%); the major component is ascribed to DHP-^{1}P and the minor to residual CPD-^{1}P.

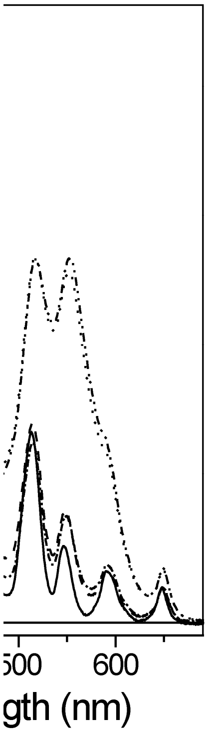
Thus, the DHP moiety quenches the porphyrin first excited singlet state significantly. The rate constant for this process is 4.9×10^8 s^{-1}. Transient absorption experiments did not allow determination of the product of this quenching. Singlet energy transfer to DHP is unlikely; the overlap of the porphyrin emission and DHP absorption spectra is poor for this endergonic (0.1 eV) process and no evidence for reverse energy transfer from DHP to P was observed. Electron transfer to form DHP$^{\bullet+}$-P$^{\bullet-}$ is thermodynamically possible, with a driving force of 0.14 eV, but no definitive evidence for the charge-separated state was seen in the transient absorption results for the DHP form of dyad **2**. It may be that the rate constant for recombination of the charge-separated state is larger than that for its formation (leading to a very low concentration at all times). Based on these observations, electron transfer to form DHP$^{\bullet+}$-P$^{\bullet-}$ seems to be the most likely quenching mechanism.

Transient absorption and emission experiments[27] on the P-DHI form of dyad **3** have revealed that the porphyrin first excited singlet state of **3c** is unquenched, and neither energy nor electron transfer between the moieties occurs. In the P-BT form **3o**, electron transfer occurs from ^{1}P-BT to yield P$^{\bullet+}$-BT$^{\bullet-}$

with a rate constant of 2.0 × 10^{10} s^{-1} (τ = 49 ps), and a quantum yield of 1.0. Recombination of $P^{\bullet+}$-$BT^{\bullet-}$ to the ground state occurs rapidly, with a rate constant of 3.4 × 10^{11} s^{-1}.

Triad 1 Absorption. The absorption spectrum of a model porphyrin is shown in Figure 3. It features a Soret band at 418 nm and Q-bands at 513, 547, 592 and 648 nm. The spectra of the various isomers of **1** resemble linear combinations of this spectrum and those of the attached photochromes, demonstrating that linkage of the moieties does not have drastic effects on the energies of the ground and first excited singlet states of any of the chromophores. In addition to the porphyrin bands, the DHP-P-DHI isomer features absorption by the photochromes in the UV, and a broad, fairly weak band at 513 nm underlying the porphyrin absorption. This band is characteristic of DHP.[26] DHI does not absorb significantly in the visible spectral region.

Irradiation of the sample with red light for 300 s photoisomerizes DHP without affecting DHI, converting the majority of the sample to CPD-P-DHI. The spectrum in the visible shows a decrease in the broad 513-nm DHP absorption, and a decrease at 366 nm, where DHP-P absorbs strongly. (P-DHI has an isosbestic point at this wavelength.)



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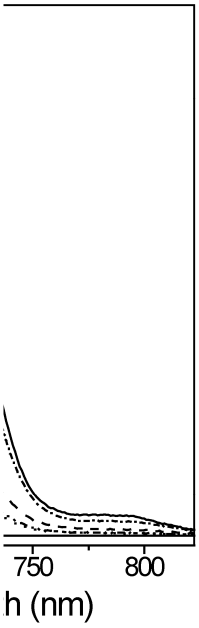
Next, the sample was exposed to 40 s of 366 nm light, followed by 300 s of red light, and the spectrum was recorded. Experiments on the model dyads have shown that the UV light causes isomerization to DHP-P-BT, and the red light then opens the DHP, leading to CPD-P-BT. Figure 3 verifies that this has occurred, revealing a strong, broad absorption of BT[27] between 440 and 650 nm, with a maximum at ~530 nm, that underlies the porphyrin Q-bands. It will also be noted that there is little absorbance change at 366 nm, verifying that there has been no net isomerization of CPD back to the DHP form.

Finally, the sample was exposed to 40 s of 366 nm light followed by 5 s of 254 nm radiation. Studies with model compounds **2** and **3** have shown that the 366 nm light opens the DHI to a photostationary state containing about 85% BT, and partially closes the CPD, giving a ratio of 45:55 CPD:DHP. The 254 nm light then closes most of the remaining CPD to the DHP form. Thus, the resulting state is mainly DHP-P-BT. This is illustrated in Figure 3, which shows the strong BT absorbance in the 530 nm region in addition to an increased absorption at 366 nm corresponding to DHP.

Figure 3 shows that by using the wavelengths and exposure times listed above, a sample of triad **1** may be photoisomerized into any of the four isomeric forms shown in Figure 1. This is key to the operation of the logic gates. Of course, in most cases, a given sample is actually a mixture of all four forms, with a preponderance of one isomer. This cannot be avoided, especially when UV irradiation is employed, as each photochrome reaches a photostationary state. In the case of DHP-P-BT, the 300 s of red light irradiation is enough to convert essentially all of the DHP to the CPD form while closing less than 10% of the BT to the DHI form. It was also determined that exposure of the sample to 55° C for 30 min will thermally close virtually all of the BT isomers to the DHI form, but close no more than 15% of the CPD isomers to the DHP form. Alternatively, exposure to the pulsed IR laser (1064 nm) for 3 h converts 85% of BT to the DHI form. Although both CPD and DHI are both isomerized by 254 nm irradiation, the two-wavelength (254 and 366 nm) sequence mentioned above was employed to reduce photodecomposition of the DHI moiety.

Triad 1 Emission. The conclusions concerning the various states of **1** deduced above from absorption spectra and model compound studies is verified by steady-state and time-resolved emission studies. Figure 4 shows the emission spectra of solutions enriched in the various forms of **1**, prepared as discussed above. The spectrum of the model porphyrin 5,15-bis(4-methoxycarbonylphenyl)-10,20-bis(2,4,6-trimethylphenyl)porphyrin is shown at a convenient amplitude for comparison. It is clear that the emission in this spectral region is dominated by the porphyrin moiety. It is also evident that emission is strong from the CPD-P-DHI form of the triad, where porphyrin quenching by photochromes does not occur. Converting the CPD to the DHP form results in significant quenching, as expected from the behavior of model compound **2**. Alternatively, conversion of the DHI to the BT isomer leads to even more quenching, and this too is expected given the behavior of the model compound **3**. The most quenching is observed when both DHP and BT are present in the molecule.

Further confirmation of the source of the fluorescence quenching comes from time resolved measurements. Excitation of 2-methyltetrahydrofuran solutions (not deoxygenated) of several of the isomers, prepared as discussed above, was at 590 nm with ca. 9-ps laser pulses, and detection was at 650 nm. The model porphyrin yielded a single exponential decay of 10.16 ns (χ^2 = 1.18), which is characteristic of the lifetime of the first excited singlet state of model porphyrins in aerated solutions. Similar experiments with a solution enriched in the CPD-P-BT triad yielded a decay that was fitted with three exponential



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components (χ^2 = 1.05) of 43 ps (85% of the total initial amplitude), 470 ps (2%) and 12 ns (13%). The 43 ps component is ascribed to quenching of the porphyrin excited state by photoinduced electron transfer to the BT to give the CPD-P$^{\bullet+}$-BT$^{\bullet-}$ charge-separated state. It is similar to the 49 ps time constant observed for quenching of P by BT in model dyad **3**. The 12 ns component is assigned to the fraction of the molecules still in the CPD-P-DHI form, and the minor component to an impurity. Similar studies of a solution enriched in the DHP-P-DHI form (χ^2 = 1.00) yielded two exponential components of 1.55 ns (60%) and 11.1 ns (40%). The 1.55 ns component is assigned to quenching of P by DHP, and agrees reasonably well with the time constant of 1.76 ns measured for dyad **2**. The 11.1 ns component is due to some of the molecules that remain as CPD-P-DHI. The relatively high amplitude of this component (40%) is a consequence of the conversion of DHP to CPD by the excitation light at 590 nm employed in this experiment.

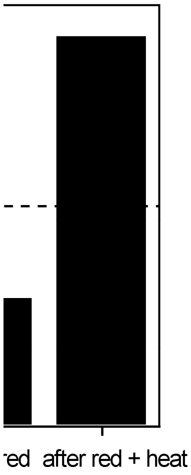
Taken together, the time-resolved fluorescence studies demonstrate that the fluorescence quenching behavior observed in the various forms of the triad may be ascribed to quenching processes similar to those observed in the respective dyads **2** and **3**.

AND Gate Function. The truth table for an AND gate is shown in the first three columns of Table 1. The gate features two inputs, *A* and *B*, and an output. The output, normally *off* (0 in the table), is switched *on* (1 in the table) only if *both* inputs are turned on. To use triad **1** as a molecular AND gate, input *A* is defined as heating for 30 min at 55° C (or pulsed IR laser irradiation for 3h), and input *B* is red light irradiation for 300 s, as discussed above. The output is strong fluorescence from the porphyrin. The molecule, dissolved in 2-methyltetrahydrofuran, is initially set

Table 1. Truth table for AND gate

input *A* (heat or IR)	input *B* (red light)	output (porphyrin fluorescence)	state of **1**
0	0	0	DHP-P-BT
1	0	0	DHP-P-DHI
0	1	0	CPD-P-BT
1	1	1	CPD-P-DHI

in the state DHP-P-BT, *i.e.*, the form where both photochromes quench porphyrin fluorescence. The molecule was converted to this initial state, and reset after each logic operation, by irradiation with 40 s of light at 366 nm followed by 5 s of 254 nm light. With neither input on, fluorescence output is below a threshold level, and the AND gate remains *off*. If input *A* is applied, BT is converted to DHI, yielding DHP-P-DHI. The DHI does not quench porphyrin fluorescence, but the DHP is still an active quencher, so the gate output remains *off*. Alternatively, if input *B* is turned on, DHP is isomerized to CPD, which does not quench fluorescence. But BT is essentially unaffected by this amount of red light, and continues to quench porphyrin fluorescence, maintaining the gate in the *off* state. Finally, applying both inputs isomerizes both photochromes, yielding CPD-P-DHI. Neither photochrome quenches the porphyrin excited singlet state, and strong fluorescence is observed, signaling that the output is in the *on* state. Thus, the molecule meets the criteria for an AND gate. The experimental porphyrin emission intensities at 720 nm are shown in Figure 5.



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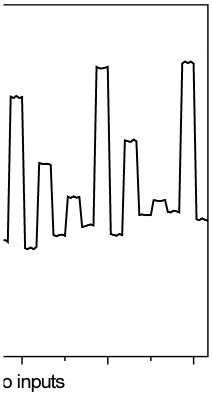

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The operation of the gate through several cycles is illustrated in Figure 6, wherein the porphyrin emission intensity is indicated following each input. The actual signal-to-noise obtained is evident from these data. Following each measurement, the gate was reset to its initial state and another measurement taken prior to initializing the next input. It is clear that although the gate may be cycled many times while still retaining a sufficient signal-to-noise ratio to allow detection of the state of the output, the emission intensity in the initial state increases following each reset operation. This is due for the most part to photodecomposition of the dihydroindolizine moiety.

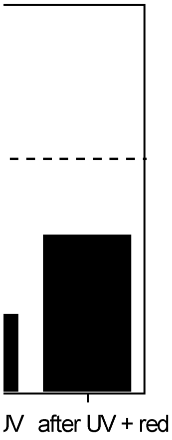
INHIBIT Gate Function. By using a suitable initial state and inputs, triad **1** can also be employed as an INHIBIT gate. An INHIBIT gate can be considered as an AND gate with one input inverted by a NOT function. The INHIBIT gate (Table 2) has two inputs and an output. When neither input is on, the gate is *off*. Switching on input *A* turns the gate *on*. However, turning on input *B* does not switch the gate *on*. In addition, switching both inputs on leaves the gate in the *off* position. Thus, input *B* inhibits the gate from responding to input *A*.

Table 2. Truth table for INHIBIT gate

input *A* (red light)	input *B* (UV light)	output (porphyrin fluorescence)	state of **1**
0	0	0	DHP-P-DHI
1	0	1	CPD-P-DHI
0	1	0	DHP-P-BT
1	1	0	CPD-P-BT

When triad **1** is used as an INHIBIT gate, it is set initially in the state DHP-P-DHI. This was done by exposing the sample dissolved in 2-methyltetrahydrofuran to 40 s of 366 nm irradiation, 5 s of 254 nm irradiation, and then 30 min at 55° C. Alternatively, exposure to IR laser pulses for 3 h could be substituted for the heating step. In the initial, DHP-P-DHI state, the porphyrin fluorescence, which comprises the output of the gate, is quenched by DHP and the gate is *off*. Input *A* is red light for 300 s. This isomerizes DHP, leading to CPD-P-DHI. Porphyrin fluorescence is not quenched in this state, and the gate is turned *on*. Input *B* is UV irradiation at 366 nm for 40 s. This converts DHP-P-DHI to DHP-P-

BT, wherein the porphyrin excited state is quenched by both photochromes, porphyrin emission is weak, and the gate remains *off*. Finally, irradiation with both red light and 366 nm light (both inputs on) isomerizes DHP, generating CPD-P-BT. In this isomer, the porphyrin fluorescence is quenched by BT, and the gate output is *off*. Between applications of the various inputs, the gate is reset to its initial condition as discussed above. Thus, the requirements for an INHIBIT gate are met.



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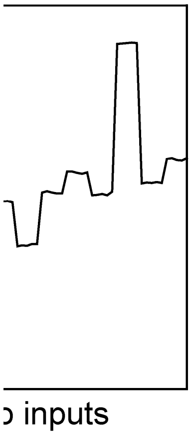

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Figure 7 shows the measured relative fluorescence emission intensity for a typical sample in the initial state and following the various combinations of inputs. It is clearly easy to distinguish between the *on* and *off* states based on porphyrin fluorescence. Figure 8 shows cycling of the INHIBIT gate. The molecule degrades more quickly in the INHIBIT mode than in the AND mode, but the signal-to-noise ratios are such that it would be possible to follow the switching performance through a substantial number of cycles.

IR Laser as an Input. As mentioned above, the application of heat via a heating block as an input can be replaced as an input signal or component of the reset operation with IR laser pulses at 1064 nm. When this was done, the performance of both the AND and INHIBIT functions was very similar to that shown in Figures 5-8, and the results are not shown here. During these experiments, the ambient temperature was 18° C, and the time constant for thermal isomerization of BT to DHI at this temperature is 244 min. When exposed to the 1064 nm laser pulses (at 10 Hz), the time constant for isomerization was reduced to 93 min. Thus, the isomerization is due, to a large extent, to the laser irradiation.

Triad **1** does not have electronic transitions at 1064 nm, and the isomerization rate is a linear function of IR laser power, ruling out possible 2-photon effects. The photonic (IR) input must cause isomerization of BT via a thermal pathway through absorption of light by the solvent or solute molecules. This heating is a local phenomenon, as the bulk sample temperature rises only slightly during irradiation. The relative rates of isomerization and thermalization of a molecule of **1** following excitation at 1064 nm are not known. The IR laser wavelength (1064 nm) was chosen for reasons of convenience, and is clearly not optimized for this particular purpose.

Discussion. It is clear from these results that triad **1** carries out the functions of an AND or INHIBIT gate, depending on the reset conditions and the nature of the inputs. The two photochromes in **1** serve to record the input history (*A* on, *B* on, *A* and *B* on). The function of the porphyrin is to correlate the responses of the two photochromes, generating outputs that are representative of the states of both photochromes as required for a given logic operation. This crucial function is possible because the porphyrin excited singlet state communicates electronically with each gate, and the porphyrin fluorescence is easily measurable. The covalent linkages joining the porphyrin to the two photochromes have been chosen in order to achieve such electronic communication while not quenching the excited states of the photochromes to the point where photoisomerization no longer occurs.

The purpose of this research was to investigate the feasibility of achieving the desired functions photochemically in a molecular system, and not to demonstrate the practicality of such a molecule in an actual technologically useful device. Nevertheless, data relevant to such an application appear in Figures 6 and 8, which indicate that under the conditions of the experiment, the triad degrades somewhat upon cycling through the various logic operations. It is clear from these data that the molecule could be cycled numerous times before the degradation reached the point that *on* and *off* responses could no longer be differentiated. However, the degradation is clearly too rapid to make the molecule useful in applications where it would have to be cycled thousands of times. Experiments on **2** and **3** have shown[26,27] that although the DHP moiety is quite resistant to photodecomposition, the DHI moiety can degrade upon repeated cycling. It is not known whether other conditions, such as rigorous degassing, employing a polymeric film or glassy solid as the solvent, etc., would slow degradation of **1** significantly, as we have not attempted to optimize performance of the system. However, we[27] and others[30] have found that photodecomposition of dihydroindolizines related to that used in this study is greatly reduced when oxygen is rigorously excluded (e.g, by freeze-pump-thaw cycles), and this was not done in the case of **1**.

The speed of response of the gates is also of interest for any potential device applications. The readout response time is on the ns time scale, as described above. The time required for isomerization of the photochromes depends, of course, on the light intensity and the temperature or IR laser flux, as appropriate. For example, the slowest step in the switching sequence for **1** above was irradiation with the pulsed IR laser for 3 h. This corresponds to 540 μs of actual irradiation time. An increased light flux would shorten the time required accordingly. In addition, the experiments were carried out in standard 1 cm cuvettes and sample sizes of ~2 mL. As the gates are of molecular dimensions, and the readout is fluorescence, which may in general be detected even with single-molecule sensitivity, it should be possible to carry out these experiments with very small volumes, and consequently shorter photoisomerization periods.

Conclusions

Triad **1** has been shown to operate as either a molecular AND logic gate or molecular INHIBIT gate, based on the choice of inputs and initial conditions. This is possible because the states of two independently-isomerizable photochromes are "sensed" by the central porphyrin, which provides an output that is based on the requirements of the gate in question. The inputs may be all photonic (although IR light is converted to thermal energy), and the output is also photonic (porphyrin fluorescence). In principle, the output could also be electronic because photoinduced electron transfer is responsible for the fluorescence quenching by BT, and likely by DHP. This approach to logic elements differs from some others in that it is based on molecules rather than materials, does not require physical access for addition of chemicals as inputs, has switching times that are not limited by bimolecular chemical reactions, and can in principle operate in media of relatively high viscosity. It is also entirely molecular in nature, whereas our previously-reported AND gate required both a molecule and a third-harmonic-generating crystal.[23] The performance of the system has not been optimized, but as described, long-term stability is limited by degradation of the DHI moiety over a period of many cycles.

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